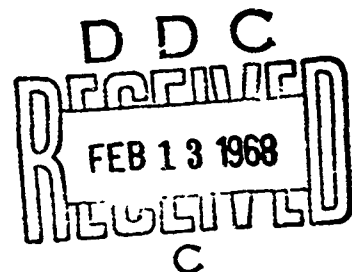OUR TECHNICAL REPORT No. 94
Project: NR 056-378
Contract: Nonr 3357(01)

OPTICAL CHARACTERIZATION OF THE ORIENTATION
OF AMORPHOUS POLYMERS AND AMORPHOUS PARTS
OF CRYSTALLINE POLYMERS

by

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September 1967

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Orientation of Crystals

The orientation of the crystals in a crystalline polymer may be
readily determined by the x-ray diffraction technique[1-7] and their average
orientation may be specified by giving orientation functions[8-16] of the sort

$$f_Q^{(2)} = \frac{3 <\cos^2 \phi_Q>_{av} - 1}{2} \tag{1}$$

where ϕ_Q is the angle between a reference axis, Q, and the stretching direc-
tion. $f_Q^{(2)}$ is zero if the axis Q is randomly oriented and is one if the axis is
perfectly oriented parallel to the stretching direction. For a more complete
description of the orientation distribution one may define higher moment
orientation functions such as the fourth-moment function

$$f_Q^{(4)} = \frac{3}{8} \left[\frac{35}{3} <\cos^4 \theta_Q>_{av} - 10 <\cos^2 \theta_Q>_{av} + 1 \right] \tag{2}$$

In general as is originally proposed by Muller[9,14] and utilized by Krigbaum, [7,17] a general orientation distribution may be represented as an expansion in spherical harmonics.

If $\xi = \cos \theta_s$ and $w(\xi) d\xi$ is the probability of finding a value of ξ between ξ and $(\xi + d\xi)$, then, for cylindrically symmetrical (uniaxial) orientation distributions

$$w(\xi) = \sum_{\ell=0}^{\infty} w_\ell P_\ell(\xi) \tag{3}$$

where $P_\ell(\xi) = P_\ell^m(\xi)$ for $m = 0$ where P_ℓ^m is the normalized associated Legendre polynomial. Only even values of need be retained for symmetrical orientation distributions. Then it follows[17] that

$$f_Q^{(2)} = \left(\frac{2}{5}\right)^{1/2} w_2 \tag{4}$$

and

$$f_Q^{(4)} = \left(\frac{2}{9}\right)^{1/2} w_4 \tag{5}$$

Thus the various orientation functions characterize the various coefficients in the spherical harmonic expansion. A complete set of $f_Q^{(1)}$ is required to completely characterize the orientation distribution.

Many physical properties of a crystalline polymer may be described in terms of these orientation functions. For example, the crystalline contribution to the birefringence of polyethylene is given by[13]

$$\Delta_c = (n_a - n_c) \, f_a^{(2)} + (n_b - n_c) \, f_b^{(2)} \tag{6}$$

where $f_a^{(2)}$ and $f_b^{(2)}$ are orientation functions for the a and b crystal axes. Similarly, the infrared dichroism of the 730 cm^{-1} absorption band of polyethylene arising from a symmetrical rocking mode for the CH_2 groups in crystals is given by

$$D_{730} = \frac{1}{2} \left[\frac{3}{2f_b^{(2)} + 1} - 1 \right] \tag{7}$$

where

$$D_{730} = \left(\frac{A_\perp}{A_{||}} \right)_{730} \tag{8}$$

and $A_\perp$ and $A_{||}$ are the absorbancies at 730 cm^{-1} for radiation polarized perpendicular and parallel to the stretching direction.

Orientation of Amorphous Regions

To specify completely the orientation of a crystalline polymer, it is necessary to describe the orientation of both crystalline and amorphous regions. An orientation function like that of Eq. (1) may be defined relative to some reference direction in the amorphous chain. For example, for polyethylene, this may be taken as an axis $\underset{\sim}{R}$ normal to the plane of the CH_2 group. If the chain is extended in the stretching direction in its planar zig-zag (trans) conformation, then $\underset{\sim}{R}$ will be parallel to the stretching direction for all CH_2 groups so f_R will be one.

The determination of f_R for such an amorphous structure cannot be accomplished as easily as for crystals. While such a structure exhibits a diffuse x-ray scattering maximum which often shows azimuthal dependence for highly oriented structures, the interpretation of such data is not straightforward. The phenomonon must be considered as a scattering process involving interference between rays scattered from all pairs of atoms both within and between polymer chains. Thus the scattering depends upon the relative orientation of pairs of chains and the way in which they pack, and is not simply related to f_Q. There has been some discussion of this problem by Millberg[18].

As with a crystalline polymer, the orientation distribution of an amorphous polymer may generally be expanded in spherical harmonics as in Eq. (3), where now $\xi = \xi_Q = \cos \theta_Q$, and a complete set of the w_ℓ's is required for complete description. The determination of all these w_ℓ's is not possible, but methods will be discussed for the determination of w_2 and w_4.

Birefringence

For a uniaxially oriented polymer, the two principal refractive indeces are n_1 in the stretching direction and n_2 in the transverse direction. The birefringence Δ is then

$$\Delta = n_1 - n_2 \qquad (9)$$

The birefringence may be related to that of the perfectly oriented polymer if it is assumed that each of the monomer units is anisotropic with polarizabilities b_1 and b_2 along and perpendicular to Q. The polarizabilities of the oriented polymer, P_1 and P_2, are then determined by the tensor addition of those of the units assuming that $(b_1 - b_2)$ is not affected by the changing internal field accompanying orientation. This gives

$$P_1 - P_2 = \sum_i (b_1 - b_2) \left[\frac{3\cos^2 \theta_{Qi} - 1}{2} \right]$$

$$= N_Q (b_1 - b_2) \int w \, (\xi, \left[\frac{3\xi^2 - 1}{2} \right] \sin \theta_Q \, d\theta_Q$$

$$= N_Q (b_1 - b_2) \, f_Q^{(2)} \qquad (10)$$

where N_Q is the number of monomer units per unit volume. Only the coefficient of the second spherical harmonic in the expansion of $w(\xi)$ remains because of the orthognality of the other terms with $(3\xi^2 - 1)/2$. Now for small values of birefringence (usually encountered)

$$\frac{\Delta}{\Delta_Q^o} = \frac{P_1 - P_2}{N_Q (b_1 - b_2)} \tag{11}$$

where Δ_Q^o is the birefringence of a hypothetical solid made from perfectly oriented monomer groups.

Thus,

$$\Delta = \Delta_Q^o \; f_Q^{(2)} \tag{12}$$

the difficulty in applying this equation lies in assigning a value of Δ_Q^o. One approach is to obtain it from the Kuhn-Grun equation for the birefringence of a rubber

$$\Delta = \frac{2\pi}{45} \frac{(n^2 + 2)^2}{n} N_c (b_1 - b_2)_s \left(\alpha^2 - \frac{1}{\alpha}\right) \tag{13}$$

where n is the average refractive index, N_c is the number of chains (sections between crosslinks) per unit volume, α is the elongation ratio and $(b_1 - b_2)_s$ is the anisotropy of a statistical segment. This can be written in the form of Eq. (12)

$$\Delta = \Delta^o_s \; f^{(2)}_s \tag{14}$$

where the limiting birefringence is obtained from $(b_1 - b_2)_s$ from the differentiated Lorenz-Lorenz equation

$$\Delta^o_s = \frac{2}{9} \; \frac{(n^2 + 2)^2}{n} \; N_s \, (b_1 - b_2)_s \tag{15}$$

where N_s is the number of statistical segments per unit volume, and the orientation function of a statistical segment is

$$f^{(2)}_s = \frac{1}{5} \; \frac{N_c}{N_s} \; (\alpha^2 - \frac{1}{\alpha}) \tag{16}$$

for chains at low extensions where the Gaussian approximation use in the derivation of Eq. (13) is valid. If one assumes that Δ^o_Q, the limiting birefringence of a solid made of completely oriented chains is the same as

Δ_s^o, the limiting birefringence of a medium mode of completely oriented segments, this may be determined by a measurement on the amorphous polymer in the rubbery state provided N_c is known (which may be determined using rubber elasticity theory). Such a measurement[20] yuelds a value of $\Delta_Q^o = 0.70$. An alternate approach is evaluated Δ_Q^o from measurements of the anisotropy of n-paraffin vapors which yields a value of the same order.

As a third possibility is to assume $\Delta_{Q}^o = \Delta_c^o$, the anisotropy of a polyethylene crystal

$$\Delta_c^o = n_c - (n_a + n_b)/2 \tag{17}$$

which is equal to 0.029 using the values of crystal refractive indeces proposed by Bunn[21]. The Δ_Q^o obtained by this method is seen to be very much smaller than that obtained from the rubber elasticity or gas measurements. This indicater that perhaps Δ_Q^o is not independent of orientation and that the assymetric internal electric field arising from the highly assymetric arrangement of molecules in the crystal gives rise to a different Δ_Q^o than that in an amorphous polymer where the internal field is more assymetric[22,23,24]. Thus, in a highly oriented amorphous polymer it seems likely that the internal field may be intermediate between the two cases and the resolution of Δ into variations in f_Q and Δ_Q^o would not be easy.

In the application of the birefringence technique to amorphous polymers in the glassy state, birefringence contributions may arise from distortional as well as orientational contributions[25]. This distortional birefringence may in some cases (polystyrene, polyethyl acrylate) be of opposite

sign from the orientational birefringence. It arises from a different molecular response to deformation. In the rubbery state, birefringence arises from long-range chain orientation arising from changing chain conformation associated with rotation about single bonds. On the other hand, the distortional birefringence arises from short-range effects such as bond angle bending and changing internal field caused by changing van der Waal's distances between molecules. A polymeric glass may exhibit birefringence arising from both causes; there may be both frozen-in orientation as well as distortional stresses. These may often be resolved by annealing out the distortional stresses under conditions where the orientation remains.

The orientational birefringence of polymer molecules such as polystyrene and polymethyl-methacrylate is complicated in that it depends upon both the orientation of the side group as well as that of the main chain. For example, the birefringence of polystyrene is highly dependent upon the rotational angle of the phenyl group about the bond which joins it to the chain[26].

For a crystalline polymer, the total birefringence arises from the contributions of the crystalline and amorphous regions[12,27] which may be given (assuming the two-phase model) by

$$\Delta = X_c \Delta_c + (1 - X_c) \Delta_a + \Delta_f \tag{18}$$

X_c is the volume fraction crystallinity, Δ_c is the crystalline contribution given by equations like Eq. (6). Δ_a is the amorphous birefringence and Δ_f is the form birefringence which arises from the effect of the crystal-amorphous

phase boundary on the electrical field of the light wave. This depends upon the shape of the boundary and upon the refractive index difference between phases. It may be changed by swelling one of the phases by solvents of differing refractive index. By this means, Δ_f was estimated for low-density polyethylene and found to contribute 5-10% of the total birefringence[28]. In cases where there voids or where a polymer is a polyblend such that there are phase boundaries of high refractive index difference, Δ_f may be much greater.

The crystalline contribution to the birefringence of polyethylene may be determined using Eq. (3) with crystal refractive indeces and orientation functions determined by x-ray diffraction. Upon subtracting this from the total birefringence, the amorphous orientation function variation of Fig. (1) is obtained[27,29]. where the upper (Bunn-Daubeny) curve is obtained using $\Delta_Q^o = \Delta_c^o$ while the lower (Denbigh) curve is obtained using essentially $\Delta_Q^o = \Delta_s^o$. The truth probably lies between the two curves, with this author (RSS) favoring values closer to the lower curve. In any case, it is noted that the values are relatively high corresponding to values of the order of $f_Q = 0.1$ for a 100% elongated sample. This is much greater orientation than found for completely amorphous polymers and could be interpreted as resulting from fairly short amorphous chain sequences between crystals.

The negative values of amorphous orientation at low elongations are somewhat uncertain as the precision of the measurement of the x-ray orientation functions at low elongations is not great. More recent measurements by Fujino, Kawai, Oda and Maedae[30], and by Yamada and Desper in this laboratory[31] do not indicate negative amorphous orientation in agreement with infrared data to be presented later.

Similar results for the orientation of amorphous regions of poly-propylene have been obtained by Samuels[32]. In this case, to obtain values of Δ^O_{cryst} and Δ^C_{am} the orientation functions for the crystals were obtained from x-ray measurements and were then combined with the results of sonic modulus measurements for a series of samples of differing orientations to give Δ^O_{cryst} = 0.0531 and Δ^C_{am} = 0.0468. He finds for hot drawn films an initially negative amorphous orientation at elongations less than 100% which then becomes positive at higher elongation contributing to the birefringence an amount which is about 40% of the crystalline contribution.

Dichroism

If the parallel dichroism of a band in the infrared, visible, or ultraviolet spectra of a molecule is defined by

$$D = A_{||} / A_{\perp} \tag{18}$$

[note: this is the reciprocal of the perpendicular dichroism defined by Eq. (8)], then one may generally write[33]

$$f^{(2)}_Q = \frac{D-1}{D+2} \frac{D_o + 2}{D_o - 1} \tag{19}$$

where D_o is given by

$$D_o = 2\cot^2 \phi_Q \qquad (20)$$

where ϕ_Q is the angle between the reference axis, $\underset{\sim}{Q}$, and the transition moment direction $\underset{\sim}{M}$ for the absorption. Eq. (7) is a special case of this equation. It is noted that dichroism, like birefringence, depends only upon $f_Q^{(2)}$, proportional to the coefficient of the second spherical harmonic of the orientation distribution. It is possible to find absorption bands which are associated with crystalline and with amorphous regions of polymers and to separately characterize their orientation. A comparison of the orientation functions of the a, b, and c crystal axes of low-density polyethylene $\left[f_\alpha^{(2)}, f_\beta^{(2)}, \text{and } f_\epsilon^{(2)} \right]$ obtained by x-ray diffraction (curves)[29] with the values of f_α obtained from infrared dichroism obtained using the 730 cm^{-1} and 1894 cm^{-1} bands (points) is given in Fig. (2)[34]. For both of these bands, $\underset{\sim}{M}$ is parallel to the reference axis $\underset{\sim}{Q}$ (the a crystal axis) so $\phi_Q = 0^o$, and $D_o = \infty$

$$f_\alpha^{(2)} = \frac{D-1}{D+2} \qquad (21)$$

Both of these bands are due to crystalline contributions[35-41]. The crystalline nature of the 1894 cm^{-1} band has been recently demonstrated by[34] (1) plotting the extinction coefficient of this band against degree of crystallinity X_c, the extinction coefficient extrapolates to zero at $X_c = 0$. (2) plotting the extinction coefficient against temperature. It becomes zero at the crystalline melting point.

It is seen that there is good agreement between the x-ray and infra-

red values of $f^{(2)}_\alpha$ for the 1894 cm^{-1} band but not too good agreement using the 730 cm^{-1} band. [It is believed that the data reported here for the 730 cm^{-1} band is better than that previously reported[12] (which indicated better agreement) in that better procedures were used for the x-ray determination of orientation functions]. The discrepancy for the 730 cm^{-1} band is believed a result of the intensity at this wavelength not being a pure band but possibly containing contributions due to (1) overlap with the 720 cm^{-1} band which is partly amorphous and partly crystalline with M along the a axis, and (2) overlap with a broad 745 cm^{-1} band of amorphous origin[37] (3) coupling of a defect with the lattice modes[42]. Also, lack of uniformity of the thin films necessary because of the high absorption at 730 cm^{-1} probably resulted in experimental error in the measurement of D_{730}.

For measurement of the amorphous orientation of polyethylene, use may be made of bands at 2016 cm^{-1}, 1078 cm^{-1}, 1368 cm^{-1} and 1303 cm^{-1}. All of these bands arise from amorphous components[35-41]. The 1303 cm^{-1}, 1352 cm^{-1} and 1368 cm^{-1} bands have been reported to have M parallel to the chain axis[38,39], so $D_o = \infty$, while the 1078 cm^{-1} has M perpendicular to the chain axis[38] so $D_o = 0$.

The crystalline and amorphous contributions to the 2016 cm^{-1} band may be separated by observing the dependence of its extinction coefficient upon degree of crystallinity and upon temperature[34]. Then the amorphous contribution to the dichroism at 2016 cm^{-1} may be obtained from

$$D_{2016} = \frac{(\epsilon_{2016})_{\parallel} - X_c\, \epsilon^o_{c,2016}\,(1 + 2f^{(2)}_c)\,/3}{(\epsilon_{2016})_{\perp} - X_c\, \epsilon^o_{c,2016}\,(1 - f^{(2)}_c)\,/3} \qquad (22)$$

where $(\epsilon_{2016})_{||}$ and $(\epsilon_{2016})_\perp$ are the extinction coefficients for radiation

polarized parallel and perpendicular to the stretching direction at 2016 cm^{-1},

$\epsilon^0_{c,2016}$ is the crystalline contribution to the average extinction coefficient

at 2016 cm^{-1}, and $f^{(2)}_\epsilon$ is the orientation function of the crystal c axis. The

amorphous orientation function at 2016 cm^{-1} is then obtained assuming $\underset{\sim}{M}_{2016}$ is

parallel to the chain axis.

The result of determining $f^{(2)}_{am}$ as a function of extension ratio

using the dichroism of a variety of bands is shown in Fig. (3). It is seen

that the $f^{(2)}_{am}$ is very dependent upon the band used for its measurement,

ranging from relatively high values for the 2016 cm^{-1} band to very low values

for the 1303 cm^{-1} band.

The explanation of this variation is that the amorphous phase con-

sists of a variety of conformations which contribute unequally to the various

absorption bands. The absorption is not due to the motion of single CH$_2$ group,

but rather to their motion along with their neighbors. The chain may be

considered to be composed of rotational isomers, designated trans(t) if the

internal rotation angle ϕ, is 0°, gauche (+), [g(+)] if it is $+120^{\circ}$ and

g(-) if it is -120°. The various amorphous bands are associated with portions

of the polyethylene chain being in certain conformations or sequences of con-

formations. The assignments are listed in Table I.

<div align="center">

Table I - Conformational Assignments
of Polyethylene Bands

</div>

Band (cm^{-1})	Assignment	Reference
1303	g	35, 38
1368	g t g	37
1078	g + t	35
2016 (am)	t t t	*
720 (am)	t t t t	37

It is noted the bands giving greatest amorphous orientation are those assigned to a more extended series of trans conformations while that showing the lowest $f_{am}^{(2)}$ is a gauche band. The orientation functions determined from infrared dichroism are, therefore, not average orientation functions of the entire chain but rather averages over parts of the chain having certain conformations or sequences of conformations. These parts of the amorphous chain orient differently. If one compares chains oriented to different extents, it is more probable that a trans (or sequence of trans) conformation will be found in a more highly oriented chain and that gauche conformations will be found in those having lower orientation.

It is apparent that upon stretching an amorphous polymer, chains will rotate so that their displacement vectors will become parallel to the stretching direction and will extend. The r.m.s. end-to-end length of a chain depends upon the conformation sequence. The most highly extended chain

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*Tentative assignment based upon high dichroism and upon being a combination band between 720 cm^{-1} band and 1295 cm^{-1} raman active band[33,39].

is that having all trans conformations and this one will contribute most to the absorption at 2015 cm^{-1} and 720 cm^{-1}.

Thus, the infrared dichroism method is capable of describing amorphous orientation in more detail than is contained in a single orientation function, so that perhaps one should define a family of orientation functions in which a typical member might, for example, be designated $f^{(2)}_{gtg}$ to represent the orientation of a methylene group, of the central monomer unit in a sequence of three monomer units with the conformational sequence, g t g. The complete specification of the orientation of a chain requires the specification of all possible sequences. However, to the approximation that long-range interactions may be neglected, it is of sufficient accuracy to consider such functions up to sequences of three conformations. Lower order function can then be expressed in terms of higher order ones. Thus

$$f^{(2)}_t = p_{ttt} \; f^{(2)}_{ttt} \; + \; 2p_{ttg} \; f^{(2)}_{ttg}$$

$$+ \; p_{gtg} \; f^{(2)}_{gtg} \tag{23}$$

where, for example, p_{ttg} is the probability that if sequences of methylenes in trans conformation are examined the central trans group will be flanked by a trans on one side and a gauche on the other. To the extent that internal rotation angles are independent

$$p_{t\,t\,g} = p_t^2\, p_g \qquad (24)$$

If rotations interact, it should be possible to interrelate sequence probabilities using Markoff statistics and to relate these probabilities to the r.m.s. end-to-end of the chain. Furthermore, it should be possible to calculate such functions $f_{i\,j\,k}^{(2)}$ in terms of the length and orientation of the chain displacement vectors.

To the approximation that the anisotropy of CH_2 group is independent of chain conformation, the orientation function to be used in Eq. (12) should be the average orientation function $f_Q^{(2)}$, where

$$f_Q^{(2)} = \sum_{i,j,k} p_{i,j,k}\, f_{i,j,k}^{(2)} \qquad (25)$$

It may well be, however, that in view of the apparent effect of internal field upon anisotropy, the value of Δ_Q^o may depend upon local chain conformation[43,44]. To the extent that only nearest neighbor interactions are considered, Eq. (12) might be replaced by

$$\Delta_{am} = p_{t\,t}\, f_{am,\,t,t}^{(2)}\, \Delta_{am,\,t\,t}^o + p_{g\,t}\, f_{am}^{(2)}\, \Delta_{am,\,g\,t}^o$$

$$+ p_{g\,g}\, f_{am,\,g\,g}\, \Delta_{am,\,g\,g}^o \qquad (26)$$

where $f^{(2)}_{am, t\ t}$, $f^{(2)}_{am, g\ t}$ and $f^{(2)}_{am,\ g\ g}$ are orientation functions for CH_2 group where the neighboring CH_2 groups are in t t, g t and g g conformations. $\Delta^o_{am,\ i\ j}$ is the corresponding anisotropy (per unit volume) of the CH_2 group and is given by

$$\Delta^o_{am,\ i\ j} = \Delta^o_Q + \Delta'_{i\ j} \tag{27}$$

where Δ^o_Q is the anisotropy of the isolated CH_2 group and $\Delta'_{i\ j}$ represents the perturbation of the anisotropy arising from the internal field of the nearest neighbor CH_2 groups on the same chain which are in the ith and j^{th} conformation (where i and j may be t or g). A more accurate treatment would include further neighbor interactions and contributions from CH_2 groups on neighboring chains. $\Delta'_{i\ j}$ may be estimated from theoretical calculations[43,44,45] or may be deduced from measurements on structures of known conformational population and orientation.

The value of $f^{(2)}_{am}$ obtained from the amorphous contribution to the dichroism at 720 cm^{-1} is not induced in Fig. (3) but is presented separately in Fig. (4). It is noted that this value exhibits the negative amorphous orientation at low elongations previously reported. The more recent and reliable measurements of $f^{(2)}_{am}$ determined from other bands which are reported here indicate that the negative values should be viewed with suspicion. It is noted that in order to calculate $f^{(2)}_{am,720}$, it is necessary to extract $D_{am,720}$ from the measured total dichroism by separating out the crystalline contribution using

$$D_{am,720} = \frac{(\epsilon_{720})_{||} - (\epsilon_{730})_{\perp} \; (1 + 2 \, f_{\beta}^{(2)}) \; / \; (1 - f_{\alpha}^{(2)})}{(\epsilon_{720})_{\perp} - (\epsilon_{730})_{\perp} \; (1 - f_{\beta}) \; / \; (1 - f_{\alpha})} \qquad (28)$$

where $(\epsilon_{720})_{||}$, for example, is the extinction coefficient at 720 cm^{-1} for radiation polarized parallel to the stretching direction. This requires the use of both the orientation functions $f_{\alpha}^{(2)}$ and $f_{\beta}^{(2)}$ for the a and b crystal axes. $f_{\alpha}^{(2)}$ can be obtained fairly reliably from either the x-ray measurements on the {200} reflection or from the infrared dichroism of the 730 cm^{-1} band, the two techniques agreeing with each other quite well. The x-ray diffraction determined orientation functions of Hoshino et. al.[29] plotted in Fig. (2) were used for this determination. The orientation function for the b axis cannot be determined directly from infrared dichroism and its determination from x-ray results on the weaker {020} reflection is subject to error. Also, one finds that $f_{\beta}^{(2)}$ is much more dependent upon polymer type and preparation conditions than is $f_{\alpha}^{(2)}$[29]. Also, Eq. (28) requires use of the extinction coefficient at 730 cm^{-1}. The equation assumes that this 730 cm^{-1} is a pure band polarized along the a crystal axis, an assumption which is now believed uncertain as previously discussed in this paper. In view of this $f_{am,720}^{(2)}$ was recalculated using the $f_{\beta}^{(2)}$ given by Kawai and co-workers[15]. It is seen that the negative value of $f_{am,720}^{(2)}$ is no longer obtained. The values of $f_{am,720}^{(2)}$ at higher elongation are large in agreement with the tentative (t t t t) conformational assignment of this band in Table I, and in approximate agreement with the values for the proposed trans amorphous contribution to the 2016 cm^{-1} band.

One might regard the highly trans amorphous conformations proposed

for the 720 cm^{-1} and 2016 cm^{-1} contributions as structure approaching that of the crystal. The distinction between such extended amorphous conformations and the structure in small highly defective crystals becomes nebulous. From this point of view that these bands may represent contributions of states of intermediate order between that of the crystal and the amorphous states, it is not surprising that they exhibit large dichroism, not very much less than that of the crystalline bands.

Another feature of the amorphous orientation function curves of Fig. (3) that might be noted is the leveling off of these curves followed by upward curvature at higher extensions somewhat reminiscent of the upward curvature of stress-strain curves of crosslinked rubbers at high extensions. The upward curvature of the stress-strain curve is associated with the non-gaussian behavior of the chains as they approach limiting elongation. On the basis of the statistical segment model

$$R_\infty \, / \, R_{rms} = N^{1/2} \tag{29}$$

where R_∞ is the completely extended length of the chain R_{rms} is the r.m.s. length of the free chain, and N is the number of statistical segments. Assuming that the upward curvature occurs in the stress-strain curve when R approaches R_∞ and that the extension ratio $L \, / \, L_o = R \, / \, R_\infty$, one would conclude that the upward curvature would occur when $L \, / \, L_o = N^{1/2}$. Since the upward curvature is seen to occur at about $L \, / \, L_o = 2$, this would indicate about four statistical segments in the amorphous chain between crystals.

Visible Dichroism of Dyed Polymers

A technique which has been used to determine orientation is to measure the dichroism of a dye which is dichroic at visible wavelengths and is incorporated in the polymer structure. In such cases, one may determine $f_{am}^{(2)}$ using Eq. (19) where

$$\frac{D_o - 1}{D_o + 2} = \frac{a_1 - a_2}{3\bar{a}} f_o^{(2)} \tag{30}$$

where a_1 and a_2 are the absorbances parallel and perpendicular to the principal axis of the dye molecule, and $f_o^{(2)}$ is the orientation function of the principal axis of the dye molecule with respect to the axis of the amorphous chain. $\bar{a} = (a_1 + 2a_2)/3$, the average absorbancy of the dye. The use of this method has been discussed for polyethylene terephthalate[45] and for nylon-6[46]. By combining birefringence with visible dichroism measurements on Congo Red dyed nylon-6, the orientation of nylon-6 has been separated into crystalline and amorphous parts[48]. Yamada has attempted to use this method for polyethylene[49] by coprecipitating the polymer and the Congo Red dye from solution. It is assumed that the dye only enters the amorphous phase and characterizes its orientation. The variation of $(D - 1)/(D + 2)$ with strain for both high and low-density polyethylene is shown in Fig. (5) when it is compared with the "theory" value for high-density polyethylene which is the value of $f_{am}^{(2)}$ obtained by the combined birefringence-x-ray diffraction method. The value is not too different from the experimental $(D - 1)/(D + 2)$ indicating that the quantity $[(a_1 - a_2)/3\bar{a}] f_o^{(2)}$ is relatively constant

during deformation and not too different from unity.

Without calibration against another method, this technique of employing a dye is not reliable because of the uncertainty in the value and constancy of $f_o^{(2)}$. A better situation is that where the absorbing group is part of the polymer molecule itself. A case of this sort has been discussed by Shindo and Stein for the case of polyvinyl chloride into which polyene structures have been introduced by dehydrohalogenation[49]. The change in dichroism of such a polymer is plotted as a function of elongation in Fig. (6) wher it is compared with the birefringence change. It is clear from the structure of the polyene that $f_o^{(2)} = 1$. Also, quantum mechanical calculations of transition moments indicate that (a_2 / a_1) should be very small[50], so it should follow that

$$f_p^{(2)} = \frac{D - 1}{D - 2} \qquad (31)$$

where $f_p^{(2)}$ is the orientation function of the polyene. If $f_p^{(2)} = f_{am}^{(2)}$, the ratio of $(f_p^{(2)} / \Delta)$ should be independent of elongation. This is not found to be strictly true [Fig. (7)]. A partial explanation of this discrepancy is that the segments representative of the polyene part of the chain will be of different length from the rest. A theoretical analysis[52] has shown that for a chain composed of segments having differing size, the orientation function of the longer segments will be greater than that of the shorter. (Another complication may arise from the crystallinity of the polyvinyl chloride. Both crystalline and amorphous regions contribute to the birefringence, while the

dichroic polyene structures probably reside in amorphous regions.) It is also foundthat the dichroism at a given elongation is dependent upon the wavelength at which it is measured[49]. This has been attributed to the fact that the longer the sequence of conjugated double bonds in the polyene, the longer the wavelength of maximum absorption. The longer polyene sequences will be stiffer and be represented by longer segments, and will consequently be oriented to a greater extent at a given elongation in the non-gaussian region of behavior[53].

It is apparent that the extension of the dichroism technique to ultraviolet wavelengths, the number of possible chemical structures that absorb which are a part of or may be incorporated into polymer chains will be increased, and the dichroism technique may be used to a greater extent.

Polarization of Fluorescence

The intensity of the polarized components of fluorescent light by groups on a polymer chain have been shown to depend upon the orientation of the polymer by Nishijima and co-workers[53,54]. It may be shown that fluorescence depends upon the orientation functions $f_F^{(2)}$ and $f_F^{(4)}$ of the absorbing axis of the fluorescent dye, where $f_F^{(2)}$ is defined as in Eq. (1) and

$$f_F^{(4)} = \frac{3}{8} \left[\frac{35}{3} <\cos^4 \phi_F> - 10 <\cos^2 \phi_F> + 1 \right] \qquad (32)$$

where ϕ_F is the angle between the absorbing axis of the fluorescent group and the stretching direction.

Then[55]

$$f_F^{(2)} = \frac{3}{2} \left[\frac{I_{||} + 2I_{\perp}}{5I_u} - \frac{1}{3} \right] \tag{33}$$

and

$$f_F^{(4)} = \frac{5}{8} \left[\frac{I_{||} - 2I_{\perp}}{5I_u} + \frac{3}{5} \right] \tag{34}$$

$I_{||}$ is the component of the fluorescent intensity polarized parallel to the stretching direction, while $I_{\perp}$ is the perpendicularly polarized component. I_u is the total intensity of fluorescent light from the same volume of un-oriented material. It is assumed that the transition moment axis for absorption and emission are the same; that is, the fluorescent molecule does not change its orientation during the life time of the excited state. In the event that this requirement is not fulfilled, correction procedures are possible.

The orientation functions of the fluorescent axes are related to the orientation functions of the amorphous chain, $f_{am}^{(2)}$ and $f_{am}^{(4)}$ and the orientation functions of the fluorescent axis with respect to the chain axis, $f_o^{(2)}$ and $f_o^{(4)}$ by

$$f_F^{(2)} = f_o^{(2)} f_{am}^{(2)} \tag{35}$$

and

$$f_F^{(4)} = f_o^{(4)} f_{am}^{(4)} \tag{36}$$

The fluorescent group may be a part of the polymer molecule itself (such as a polyene group) or else may be an added group bound to the chain in some manner. In this latter case, one encounters the same uncertainty as with dichroism regarding the value and constancy of f_o. If the fluorescent group is located in the amorphous part of the structure, one then obviously measures the orientation of this part of the structure.

Thus, fluorescence is capable of giving both $f_{am}^{(2)}$ and $f_{am}^{(4)}$ and provides a more complete description of the amorphous orientation. Examples of the application of the fluorescence technique have been given by Nishajima, et. al. and Krysnewski.

Other Methods

Other methods that have been used to measure amorphous orientation are the measurement of the anisotropy of sonic modulus and of nuclear magnetic resonance.

The polarization of Raman spectra from oriented solid polymers should depend upon $f_{am}^{(2)}$ and $f_{am}^{(4)}$ as does fluorescence. It should have the advantage that the lifetime of the excited state is short so the assumption of the identity of the absorption and emission axis is probably better. Also, Raman lines, like infrared absorption bands, are associated with particular modes of vibration of the molecule and are dependent upon whether the molecule is in the crystalline or amorphous phase and upon its conformation. Consequently, it has the potential of being able to characterize both $f^{(2)}$ and $f^{(4)}$ for each conformation of the molecule. With the application of lasers for Raman spectroscopy, this important technique may soon be developed.

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FIGURES

1. The variation of amorphous orientation during the stretching of low-density polyethylene calculated using Δ°_{am} from (a) Bunn-Daubeny and (b) Denbigh [from article by R. S. Stein in Newer Methods of Polymer Characterization, B. Ke, Ed., Interscience, New York, 1964, p. 179].

2. A comparison of the variation with extension ratio of the orientation functions $f^{(2)}_\alpha$, $f^{(2)}_\beta$ and $f^{(2)}_\epsilon$ for the crystal a, b, and c axes with the values of $f^{(2)}_\alpha$ obtained from the infrared dichroism of the 730 cm^{-1} and 1894 cm^{-1} bands.

3. The determination of the variation of the amorphous orientation function from infrared dichroism using a variety of bands.

4. The variation of the amorphous orientation function with elongation for low-density polyethylene calculated using the infrared extinction coefficients for parallel and perpendicular polarization at 720 cm^{-1} and 730 cm^{-1} and using the crystal orientation functions proposed by a) Hoshino, et. al.[29] and b) Kawai, et. al[15].

5. The variation of $(D - 1) / (D + 2)$ with strain for Congo Red dyed high and low-density polyethylene compared with values of $f^{(2)}_{am}$ for high density polyethylene calculated from x-ray diffraction-birefringence data.

6. The change in dichroism and birefringence with elongation for a dehydrohalogenated polyvinyl chloride sample elongated at 60°C.

7. The variation of $[(D - 1) / (D + 2)] / \Delta$ with elongation for a dehydrohalogenated polyvinyl chloride sample elongated at 60° C.
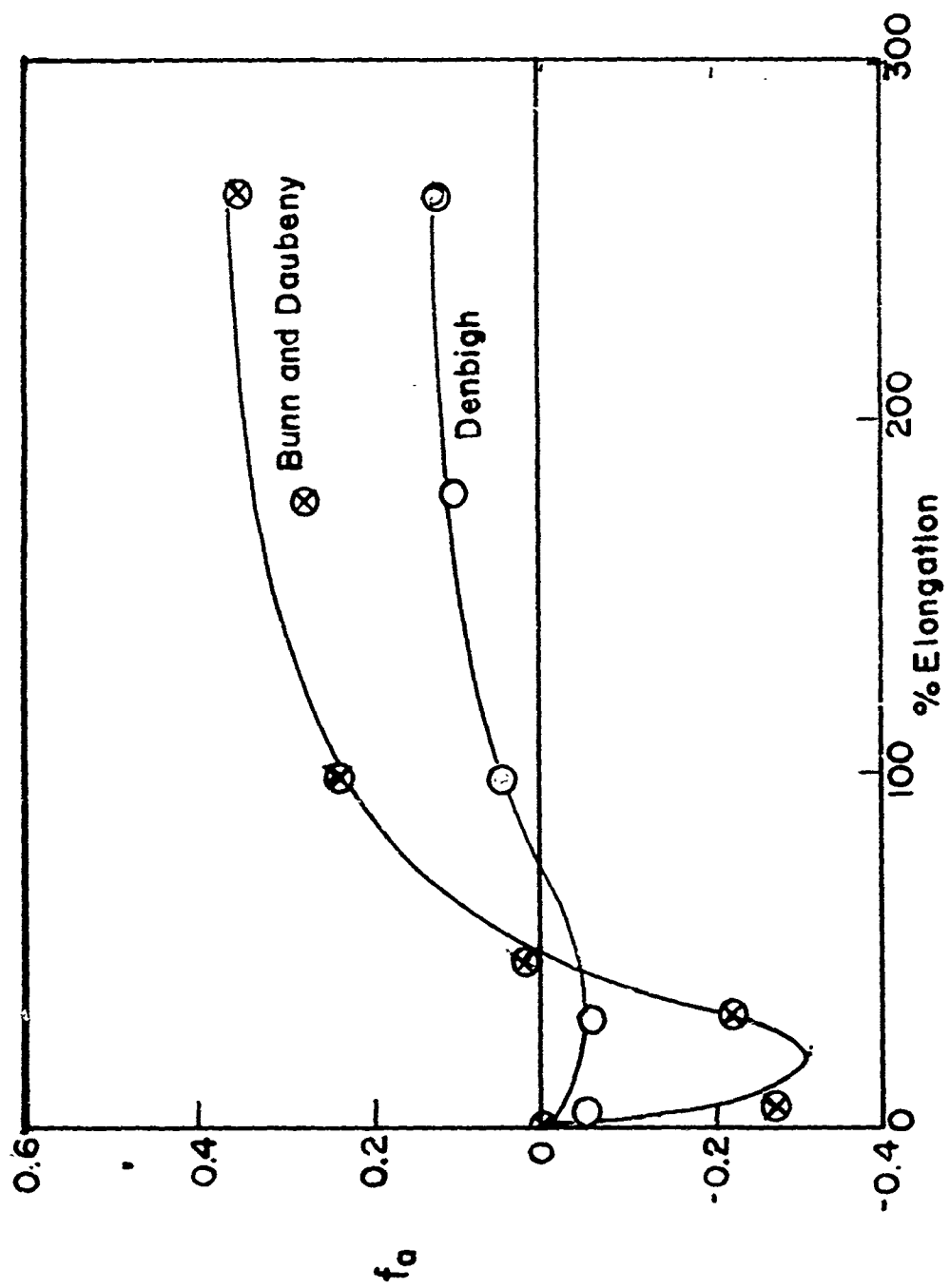
% Elongation
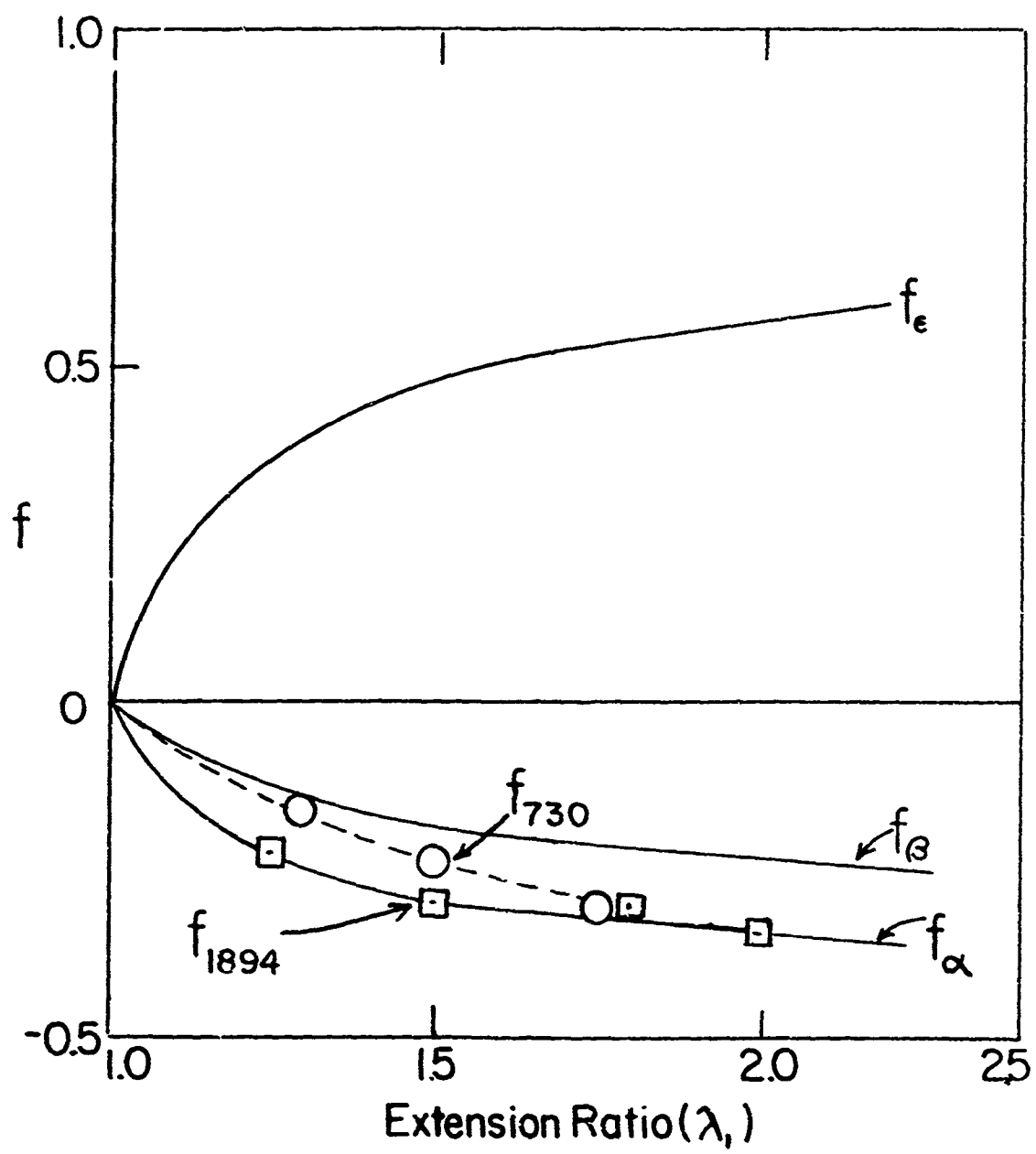
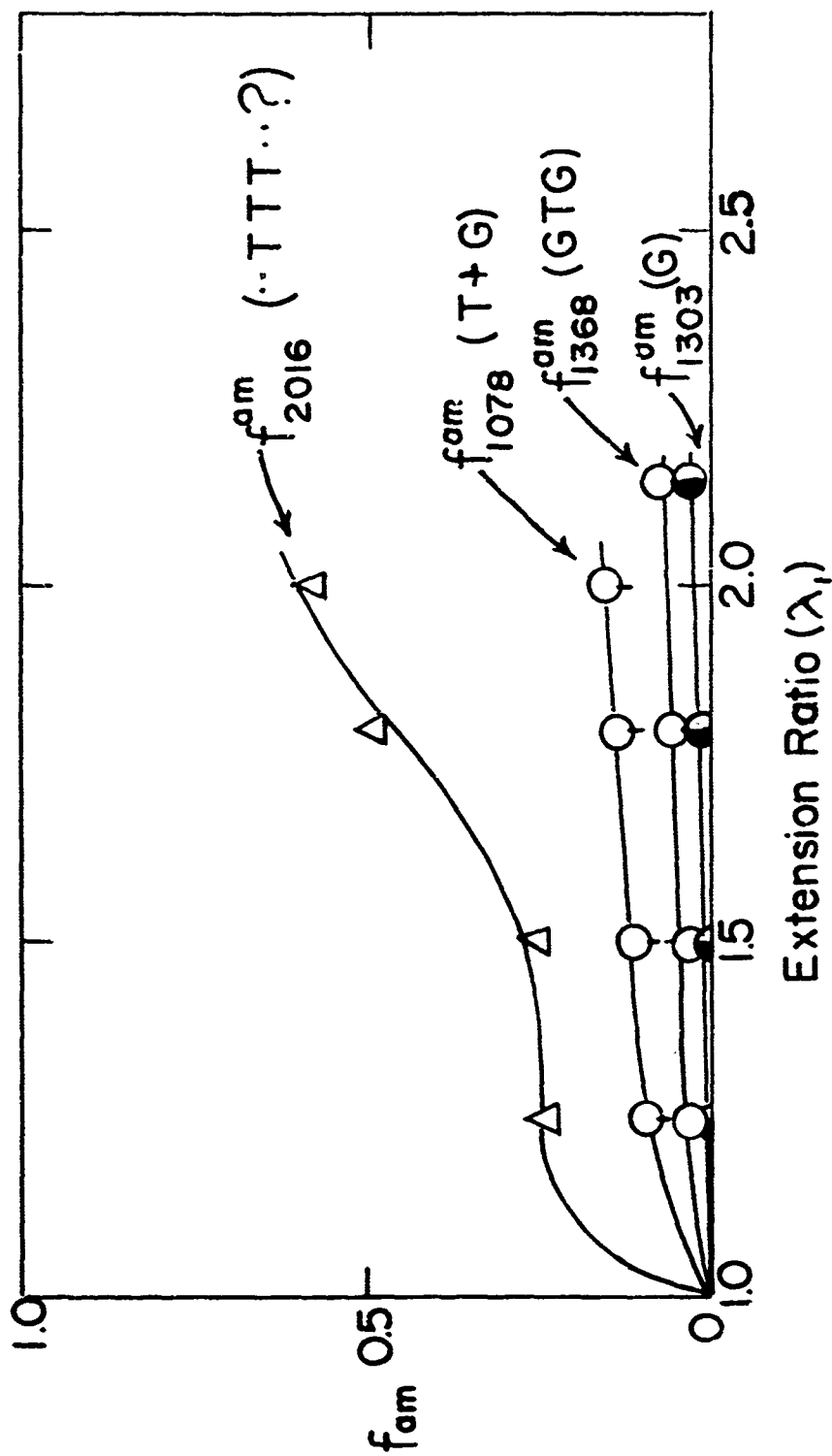Bunn and Daubeny

Denbigh

f_a

FIGURE 3

FIGURE 2

FIGURE 3

Figure axes: vertical axis labeled f_{am} with markings 1.0, 0.5, 0; horizontal axis labeled Extension Ratio (λ_i) with markings 1.5, 2.0, 2.5.

Curve labels: f^{am}_{2016} ($\cdot\cdot TTT\cdot\cdot$?), f^{am}_{1078} (T+G), f^{am}_{1368} (GTG), f^{am}_{1303} (G)

Extension Ratio (λ_1)

f_{720}^{am}
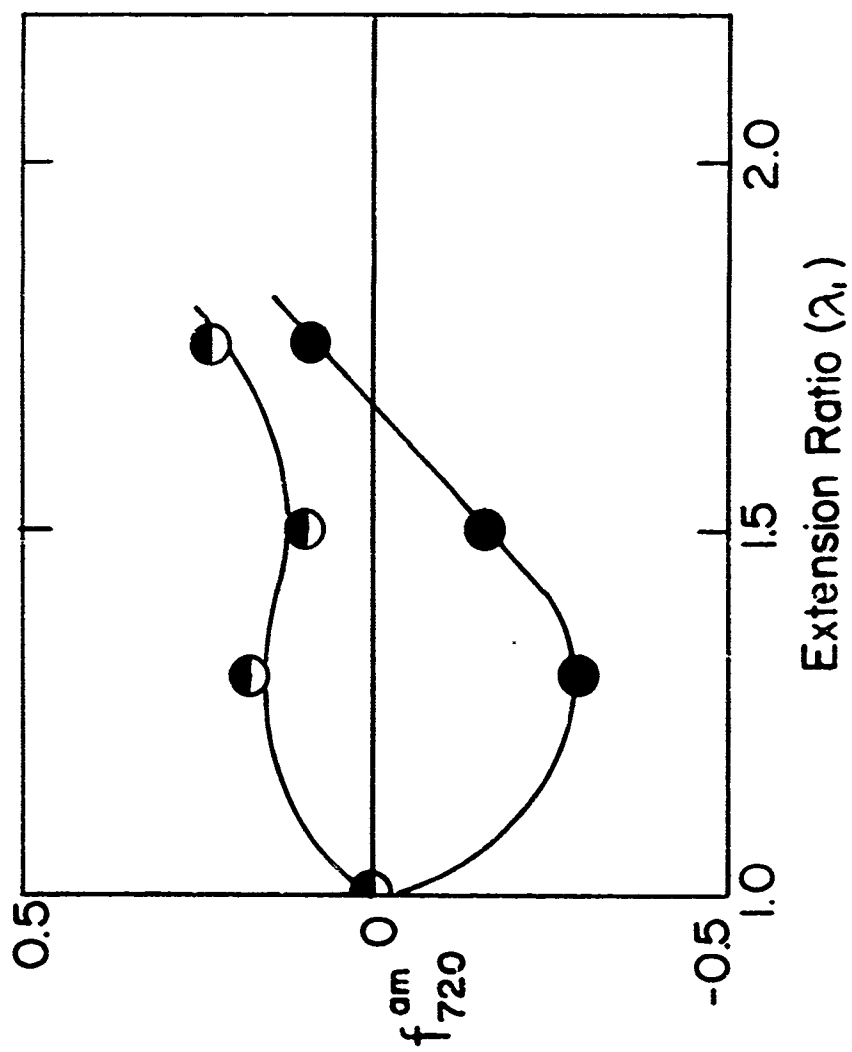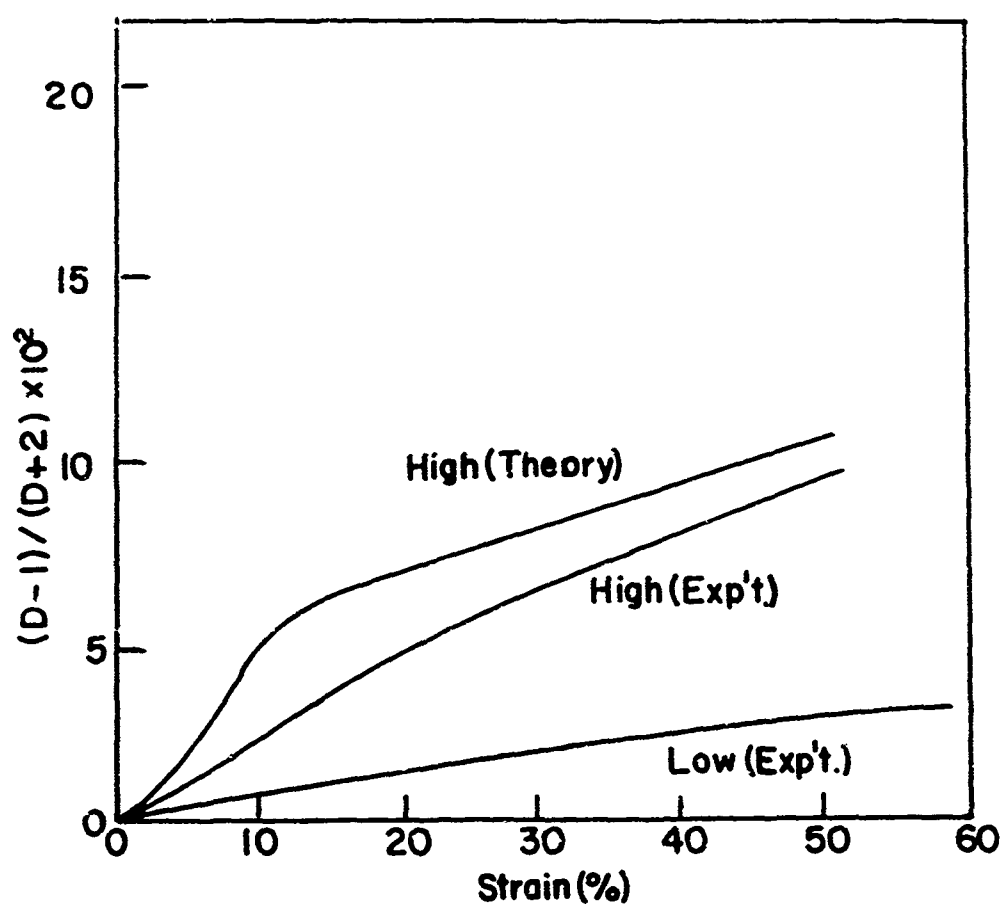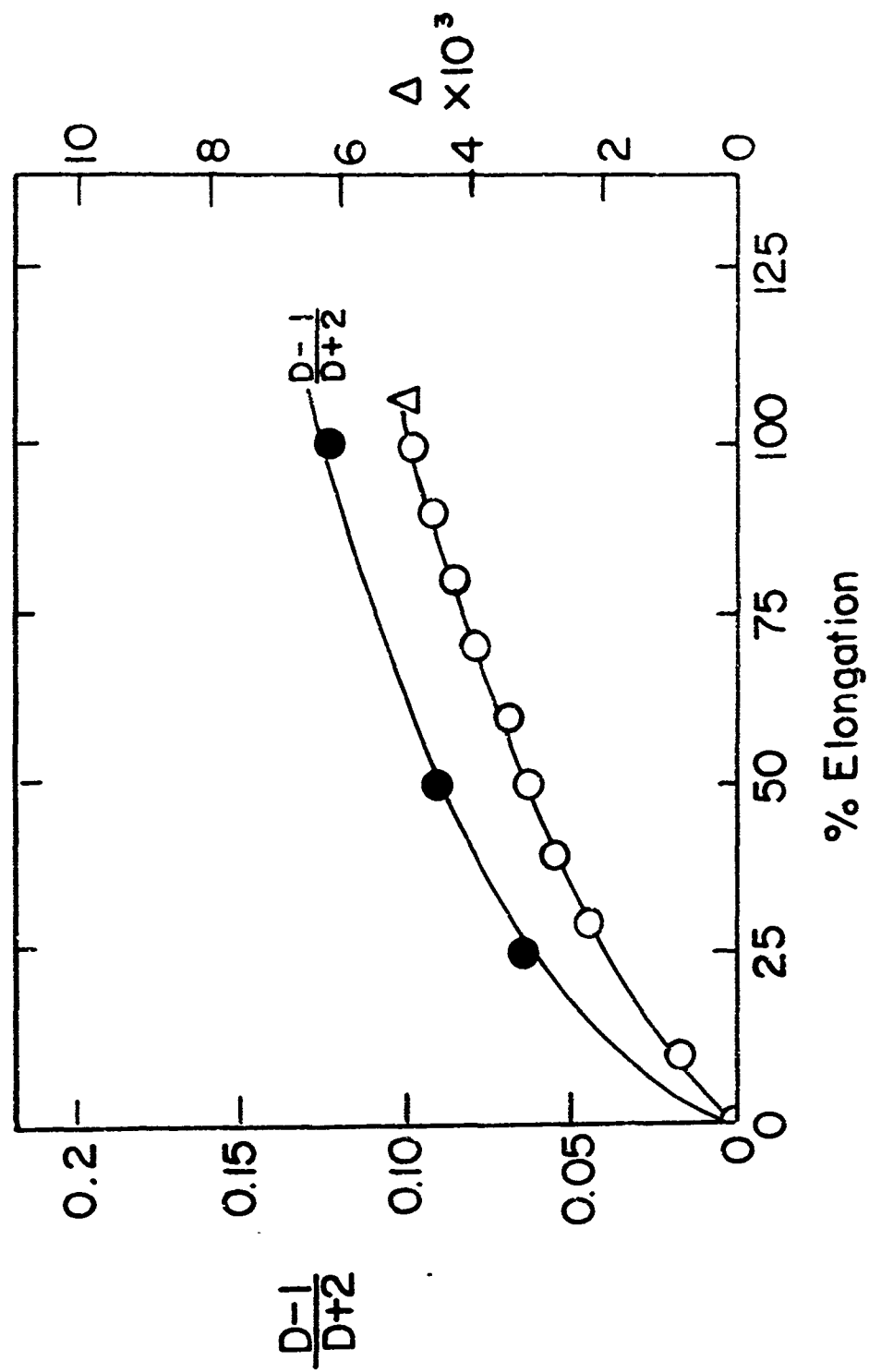
FIGURE 4

FIGURE 5

FIGURE 6
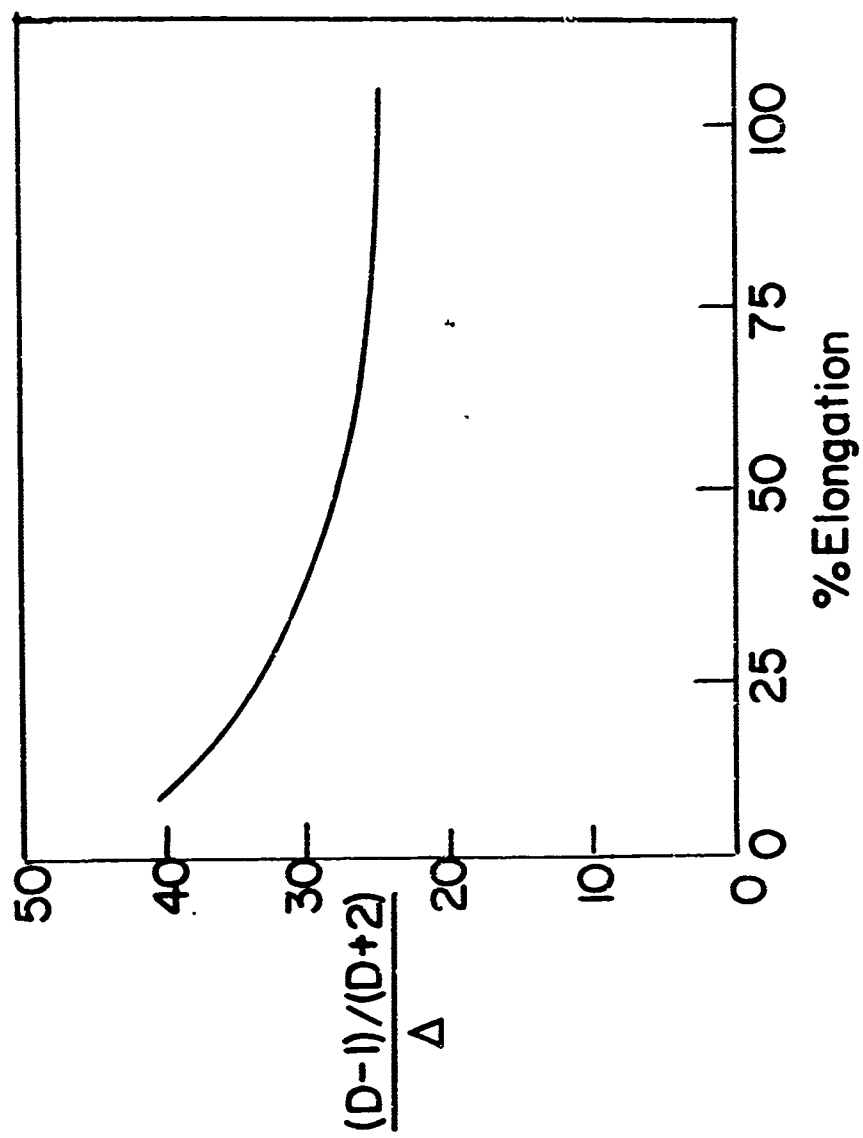
FIGURE 7

DOCUMENT CONTROL DATA - R & D		
Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified		
1. ORIGINATING ACTIVITY *(Corporate author)* Polymer Research Institute, Chemistry Department University of Massachusetts, Amherst, Massachusetts	2a. REPORT SECURITY CLASSIFICATION 2b. GROUP	
3. REPORT TITLE Optical Characterization of the Orientation of Amorphous Polymers and Amorphous Parts of Crystalline Polymers		
4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)* Technical Report		
5. AUTHOR(S) *(First name, middle initial, last name)* Read, B. E. and Stein, R. S.		
6. REPORT DATE September, 1967	7a. TOTAL NO. OF PAGES 29	7b. NO. OF REFS 55
8a. CONTRACT OR GRANT NO Nonr 3357(01) b. PROJECT NO. NR 056-378 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) 94 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	
10. DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from the Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy, Office of Naval Research, Boston Branch Office, 495 Summer Street, Boston, Massachusetts 02210	

13. ABSTRACT

Techniques for characterizing the orientation of amorphous polymers include birefringence, infrared, visible and ultraviolet dichroism, and polarization of fluorescence. The birefringence of a polymer principally results from the orientation of anisotropic segments of the polymer. The determination of absolute orientation requires a knowledge of the anisotropy of these segments. To a limited extent, this anisotropy may be calculated from bond polarizabilities.

The infrared dichroism technique does not have the precision of birefringence measurements but may offer more detailed information about the molecular orientation. Particular absorption bands characterize the orientation of transition moment directions of partical parts of the molecule. Ultraviolet and visible dichroism serve to characterize the orientation of molecules having suitable chromophoric groups. There is considerable uncertainty in this assumption, however. The polarization of fluorescent light arising from chromophoric groups on the molecule or on added dyes provides additional information about the orientation distribution in that it depends upon the mean fourth power of the cosine of the orientation angle, while the birefringence and dichroism depend upon the mean square of this angle. The orientation of the amorphous regions of crystalline polymers may be obtained from subtracting crystalline contributions to birefringence or to absorption bands by using absorption bands associated with amorphous regions or by studying the absorption or fluorescence by dyes which are absorbed by amorphous regions.

DD FORM 1473 (PAGE 1)
1 NOV 65
S/N 0101-807-6811

Unclassified
Security Classification
A-31409

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

DD FORM 1473 (BACK)
1 NOV 65

S/N 0101-807-6821

A-31409